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Surfactant free hydrothermally derived ZnO nanowires, nanorods, microrods and their characterization

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ABSTRACT

ZnO nanowires, nanorods and microrods have been prepared by an organic-free hydrothermal process using $ZnSO_4$ and $NaOH/NH_4OH$ solutions. The powder X-ray diffraction (PXRD) patterns reveal that the ZnO nano/microrods are of hexagonal wurtzite structure. The Fourier transform infrared (FT-IR) spectrum of ZnO powder shows only one significant spectroscopic band at around 417 cm^{-1} associated with the characteristic vibrational mode of Zn–O bonding. The thickness 75–300 nm for ZnO nanorods and 0.2–1.8 μm for microrods are identified from SEM/TEM images. UV–visible absorption spectra of ZnO nano/microrods show the blue shift. The UV band and green emission observed in photoluminescence (PL) spectra are due to free exciton emission and singly ionized oxygen vacancy in ZnO. Finally, the mechanism for organic-free hydrothermal synthesis of the ZnO nano/microrods is discussed.

1. Introduction

In recent years, nanostructural materials having high surface to volume ratio are of great consideration in the light of their significant potential applications in electronics, optoelectronics and catalysis [1]. Due to decrease in particle size, more and more novel properties resulting from quantum effects have been observed [2]. Nanocrystalline metal oxides play a very important role in many areas of chemistry, physics and materials science. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator characteristics [3]. Binary oxides such as ZnO, CdO, SnO_2 and In_2O_3 have distinctive properties and are now widely used as transparent conductive oxide materials and gas sensors [4]. These oxides have two unique structural features: mixed cation valencies and an adjustable oxygen deficiency, which are the bases for creating and tuning many novel materials properties [5]. ZnO is a well-known n-type wide band gap semiconductor (E_g=3.37 eV) with a large exciton binding energy of 60 meV [6]. As a result the material is transparent to visible light but not to UV light. Furthermore, ZnO is biocompatible and it exhibits both piezo- and pyroelectric properties [7]. ZnO is one of the 'hardest' materials in the II–VI compound family. As a result, ZnO devices do not suffer from dislocation degradation during operation [8]. ZnO with various morphologies such as nanowires, nanorods, nanobelts, nanotubes and nanotetrapods [9–11] have been prepared by a number of methods. Recent examples of the utilization of ZnO nanorods are found in hybrid and dye-sensitized solar cells, field-emitting cathodes, chemical sensors, low-voltage and short-wavelength electro-optical devices such as light emitting diodes and diode lasers, surface acoustic wave filters and varistors [12–18], etc. ZnO is a potential sensor of NH_3 and a photocatalyst to reduce the emission of NO_x. Due to higher solubility of ZnO in water, conventional synthesis of nanostructural materials has been considered to be especially difficult in the absence of

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any organics [14]. Template assisted sol–gel process, solvothermal, thermal evaporation, metal organic chemical vapour deposition, spray pyrolysis and microwave techniques are some of the other synthetic routes used [13,14,19–21]. Recently, ZnO nanorods are synthesized by the hydrothermal method using zinc chloride with 25% ammonia [22]. Ken Elen et al. [7] explained the various parameters in view of reducing the diameter of the ZnO nanorods synthesized by the hydrothermal method. They considered 2^{8-4} fractional factorial design of experiment which is applied to identify the important parameters that affect the average diameter of ZnO rods. The absence of an additive simplifies the procedure and the use of water as the reaction medium makes the process ecologically less demanding. Hydrothermal synthesis is becoming popular for environmental reason, since water is used as a reaction solvent than organics. This method has been widely used to prepare nanomaterials due to its simplicity, high efficiency and low cost.

Herein, we report the preparation of ZnO nano/microrods by an organic-free hydrothermal method. In order to understand the behavior of 1-D ZnO nano/microrods; the effects of mineralizer, temperature, concentration of the starting solution and the treatment time on their morphology have been investigated. The effect of particle size on the intensity of PL spectra at room temperature is investigated.

2. Experimental details

In a typical hydrothermal process [23–25], 1 g $ZnSO_4 \cdot 7H_2O$ (3.47 mmol) is dissolved in 25 ml of distilled water. To this, 10 ml of 2 M NaOH aqueous solution is introduced resulting in the formation of white precipitate. The white precipitate is stirred for 5 min with a magnetic stirrer and transferred into Teflon-lined stainless steel autoclaves with a capacity of 25 ml, sealed and maintained at different temperatures (180–200 °C) for several hours (6–24 h). Similar experiments are carried out using ammonia solution instead of NaOH. To this solution, ammonium hydroxide is added drop by drop to adjust the pH value of the solution. A white precipitate is obtained when the pH of the solution reaches 9. The obtained product is retrieved from the solution by centrifugation and washed with distilled water followed by ethanol and finally dried in air.

Zinc sulphate and sodium hydroxide are purchased from E. MERCK chemicals. Powder X-ray diffraction (XRD) data are recorded in θ–2θ coupled mode on Philips X'pert PRO X-ray diffractometer using graphite monochromatized Cu Kα radiation (λ=1.541 Å).The Fourier transform infrared spectrum of the sample is collected using Thermo Nicollet FT-IR spectrometer. The absorption spectra of the samples are measured on a UV-3101 Shimadzu visible spectrometer. Scanning electron micrograph images are taken with JEOL (JSM-840A) scanning electron microscope (SEM). Transmission electron microscopy (TEM) images are observed with a JEOL 100 CX electron microscope. Photoluminescence studies are carried out on a Perkin-Elmer LS-55 luminescence spectrometer using Xe lamp with an excitation wavelength of 325 nm at room temperature.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of the samples prepared at 180–200 °C for 6–20 h. All the diffraction peaks in the pattern can be indexed as the pure hexagonal phase of ZnO with space group $P6_3mc$. These peaks are free from $Zn(OH)_2$ impurities within the detection limit of the XRD technique. This indicates that sample is composed of wurtzite structural ZnO with the lattice constants a=3.249 and c=5.206 Å which are consistent with the values in the standard card (JCPDS 36-1451).

Fig. 2 shows the FT-IR spectrum of ZnO nanorods in the range 2000–300 cm^{-1}. There is only one significant spectroscopic band around 417 cm^{-1} associated with the characteristic vibrational mode of Zn–O bonding [26]. UV–visible spectra of the ZnO nanorods (Fig. 3(a)) and microrods (Fig. 3(b)) prepared at 200 and 180 °C for 20 h using NaOH exhibits a strong absorption between 362 and 371 nm which corresponds to a band gap of 3.43 and 3.34 eV. It is known that bulk ZnO (3.2 eV) has absorption at 387 nm in the UV–visible spectrum and is

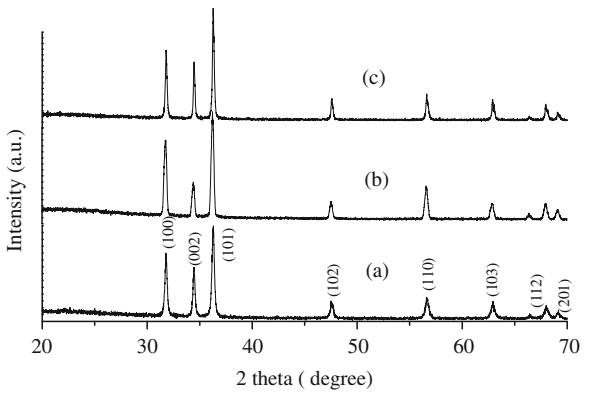

Fig. 1. Powder XRD patterns of ZnO nano/microrods prepared at (a) 180 °C for 6 h using NH_4OH; (b) 180 °C for 20 h using NaOH and (c) 200 °C for 20 h using NaOH.

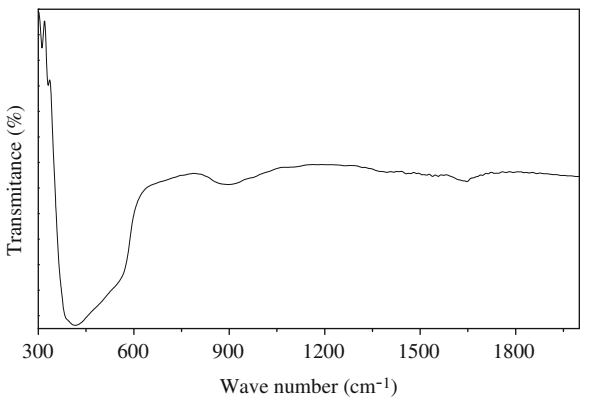

Fig. 2. FTIR spectrum of ZnO nanorods prepared at 200 °C for 20 h using NaOH.